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**A MODEL FOR VOLTAMMOGRAMS OF THE
UNDERPOTENTIAL DEPOSITION OF METALS**

by

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A MODEL FOR VOLTAMMOGRAMS OF THE UNDERPOTENTIAL DEPOSITION OF METALS

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A statistical mechanical model for adsorption is used to produce voltammograms with sharp spikes similar to those seen in recent studies of the underpotential deposition of metals onto single crystal electrodes. The voltammogram of the underpotential deposition of copper on the (111) surface of gold, which contains two spikes, can be reproduced by the model.



INTRODUCTION

Several recent studies of the underpotential deposition of metals onto single crystal electrodes have produced voltammograms (1) containing sharp spikes (2)-(7). These spikes appear to be associated with first order phase transitions which occur on the nearly perfect lattice of adsorption sites on the electrode surface.

We have recently studied a statistical mechanical model for adsorption (8)-(12) in which a solution of ions is in contact with a hard wall containing a lattice of sticky sites. The model is equivalent to a two-dimensional lattice gas in which the adsorbed atoms have an activity which is a product of a stickiness parameter and the contact density of the ions at the electrode surface. Lateral interactions are also present between neighboring adsorbed atoms.

Using eight exact coefficients from the known high and low activity series for the fraction of occupied sites (13), (14), we have constructed approximate adsorption isotherms for the model (11), (12) which are a natural extension of the Langmuir isotherm. The time derivative of the fraction of occupied sites gives a measure of the intensity of the current of the voltammogram accompanying the underpotential deposition process. The model voltammogram contains sharp spikes which are associated with first-order phase transitions which occur in the lattice gas (11), (12).

In the next section of the present paper we discuss the adsorption model and the voltammograms which are derived from it. In the final section of the paper we use the model to reproduce the voltammogram of the underpotential deposition of copper onto the (111) surface of gold. The two sharp spikes which are observed in the experimental voltammogram (3) can be reproduced by our model (12).

THE MODEL

We have recently considered a statistical mechanical model for adsorption in which a solution of ions is in contact with an electrode surface which is modeled as a smooth, hard wall with a lattice of sticky adsorption sites (11). The three-dimensional model can be shown to be equivalent to a two-dimensional lattice gas of the adsorbed atoms or ions. In the equivalent lattice gas, the adsorbate species has an activity z which is a product of a stickiness parameter λ associated with the lattice site times the density $\rho^0(0, \Psi)$ of the ions at the electrode surface, which has a dimensionless potential bias

$$\Psi = \beta e [\psi(0) - \psi_{pzc}] \quad [1]$$

Here $\beta = (kT)^{-1}$, e is the electronic charge, $\psi(0)$ is the potential at the electrode surface, and ψ_{pzc} is the potential of zero charge. We approximate the dependence of $\rho^0(0, \Psi)$ on Ψ as

$$\rho^0(0, \Psi) = \rho^0(0, 0) e^{-\mathcal{Z} \Psi} \quad [2]$$

where \mathcal{Z} is the electrovalence of the ion in solution.

The atoms of the lattice gas have a first-neighbor interaction energy $w(r)$ which is the pair-potential of mean force of the adsorbed species at a first neighbor separation r on the electrode surface. That is,

$$w(r) = -kT \ln g_2(r) \quad [3]$$

where $g_2(r)$ is the pair correlation function of the adsorbed species at a distance r .

For the lattice gas on several different lattices with lateral interactions extending only to first neighbors, many coefficients have been calculated exactly in the high z and low z power series expansions of θ , the fraction of adsorption sites which are occupied by adsorbate (13), (14). Using these series expansions, we constructed an approximant of the form

$$\theta_l = \frac{P(y^{-1})}{1 + P(y^{-1})} \quad [4]$$

which is accurate at low z , and an approximant

$$1 - \theta_h = \frac{P(y)}{1 + P(y)} \quad [5]$$

which is accurate at high z . Here $P(y)$ is a polynomial in the parameter

$$y = [z g_2(r)^{q/2}]^{-1} , \quad [6]$$

where q is the number of first neighbors to a lattice site (6 for the triangular lattice and 3 for the honeycomb lattice). The attractive lattice gas, for which $w(r) < 0$, undergoes a first-order condensation transition at $y = 1$.

The approximants θ_l and θ_h become equivalent to the Langmuir adsorption isotherm if $w(r) = 0$, i.e., if the lateral interactions are not present. These approximants are thus a natural extension to Langmuir's isotherm.

Finally, using the switching function

$$\eta(y, s) = \frac{1}{2} \{ 1 + \text{erf}[(y - 1)s] \} , \quad [7]$$

we construct a smooth, continuous approximate isotherm of the form

$$\theta = \eta(y, s)\theta_l + [1 - \eta(y, s)]\theta_h \quad [8]$$

which is accurate at both high and low z . The switching function is used to approximate the effects of surface imperfections and diffusion on the isotherm. Certainly, many different functional forms can be used for the switching function (11), (12).

A model voltammogram can be constructed from the approximate isotherm of Eq. [8], where a measure of the current intensity is given as

$$I = -\frac{\partial \theta}{\partial t} = -\frac{\partial \theta}{\partial \Psi} \frac{d\Psi}{dt} . \quad [9]$$

The current intensity given by Eq. [9] differs in sign from the intensity defined earlier (11), (12). Since the model is completely reversible, the shape of the overall voltammogram will be independent of the sign of the intensity, but using I as defined in Eq. [9] is consistent with the normal convention in which the current is positive during the stripping process, during which θ is decreasing.

A spike occurs in a plot of I versus Ψ at $y = 1$, the point where the lattice gas undergoes a first-order phase transition. From Eqs. [4]-[9] we obtain the peak height at the transition as

$$I_{y=1} = z \frac{d\Psi}{dt} [(\theta_h - \theta_l) \frac{s}{\sqrt{\pi}} - \frac{\partial \theta_l}{\partial y}]_{y=1} . \quad [10]$$

The first term, which contains the factor $\theta_h - \theta_l$, is large for isotherms at temperatures well below the critical temperature and vanishes at the critical point. The second term contains the factor $-\partial \theta_l / \partial y$, which is very small at the transition at temperatures well

below the critical temperature and is infinite at the critical point. Hence, for temperatures far from the critical temperature of the transition, the peak height is proportional to the change in surface coverage at the transition. The factor s , which is a measure of the sharpness of the switching function, is an approximate measure of the degree of perfection of the electrode surface.

It is interesting to note that the current intensity also satisfies the relationship

$$\begin{aligned} I &= z \frac{\partial \theta}{\partial z} \frac{d\Psi}{dt} \\ &= z kT \theta^2 K_T \frac{d\Psi}{dt} , \end{aligned} \quad [11]$$

where K_T is the isothermal compressibility of the equivalent two-dimensional lattice gas.

Assuming a constant sweep rate, Eq. [9] can be integrated to yield

$$\int_{\Psi_1}^{\Psi_2} I d\Psi = \frac{d\Psi}{dt} [\theta(\Psi_1) - \theta(\Psi_2)] . \quad [12]$$

Thus the area under a spike on the voltammogram is proportional to the change in surface coverage which occurs at the transition.

For temperatures well below the critical temperature, for which the peak height given by Eq. [10] is roughly proportional to s , the width of the peak must thus be inversely proportional to s , because the area under the peak, given by Eq. [12], is independent of s . Hence, a rather broad peak will result in the model voltammogram for systems in which diffusion effects or surface imperfections affect the sharpness of the phase transition.

Equation [1] at 25°C yields

$$\Psi = 38.922 V , \quad [13]$$

where V is the potential in volts. In a voltammogram plot of I , in units of $|dV/dt|$, versus V , we see from Eq. [12] that the area of the voltammogram from V_1 to V_2 is equal to $|\theta(V_1) - \theta(V_2)|$.

AN EXAMPLE VOLTAMMOGRAM

In the presence of sulfate ions, the underpotential deposition of copper on the (111) surface of gold produces a voltammogram (3) which contains two sharp spikes with areas in the approximate ratio of 2:1. This can be interpreted as resulting from a sequence of two first order phase transitions, corresponding to copper coverages of 2/3 and 1 monolayer, respectively.

We have proposed (12) that this voltammogram can result due to the following sequence of events. First, the sulfate ions occupy the sites of the triangular lattice Λ corresponding to the adsorption sites on the (111) surface of gold. Because of packing considerations, a pair of first-neighbor sites cannot be simultaneously occupied by sulfate ions. As a result, the system undergoes an order-disorder transition, equivalent to that which occurs in the hard hexagon lattice gas (15), in which one of the three triangular sublattices Λ_T of Λ is preferentially occupied by sulfate ions. This transition, which is second order, would produce a spike with an infinitesimal area which would thus not be observable as a spike in the experimental voltammogram.

As the potential is made less positive, and nearly all the sites of Λ_T are occupied by sulfate ions, the system will undergo a first-order phase transition as the copper ions are adsorbed onto the vacant sites of Λ , which form a honeycomb lattice Λ_H . Following the development of the previous section, the contribution to the adsorption isotherm due to this process is given as

$$\theta_H = \eta(y_H, s_H)\theta_{H,l} + [1 - \eta(y_H, s_H)]\theta_{H,h}, \quad [14]$$

where $q = 3$ in Eq. [6], λ_H is the stickiness parameter at the sites of Λ_H , and the lateral interaction energy is $w(d)$, d being the first neighbor separation in Λ_H and in Λ .

As the potential becomes less positive, the copper ions then replace the sulfate ions and occupy the sites of the triangular lattice Λ_T , thereby completing the formation of a copper monolayer on Λ . The portion of the adsorption isotherm due to this process is given by our model as

$$\theta_T = \eta(y_T, s_T)\theta_{T,l} + [1 - \eta(y_T, s_T)]\theta_{T,h}, \quad [15]$$

where $q = 6$ in Eq. [6], λ_T is the stickiness parameter at the sites of Λ_T , and $w(\sqrt{3}d)$ is the interaction energy between copper atoms on neighboring sites of Λ_T .

The full adsorption isotherm is then given as

$$\theta = \frac{2}{3}\theta_H + \frac{1}{3}\theta_T. \quad [16]$$

If the temperature is well below the critical temperatures for the first order transitions on Λ_H and Λ_T , then the resulting voltammogram will contain two spikes with areas in the ratio of 2:1. The resulting model voltammogram, a plot of I versus V where I is in units of $|dV/dt|$, is illustrated in Fig. 1 for the choice of parameters

$$\beta = 2,$$

$$\lambda_T \rho^0(0, 0) = 9.1,$$

$$\lambda_H \rho^0(0, 0) = 5.2 \times 10^5,$$

$$g_2^0(d) = 14,$$

$$g_2^0(\sqrt{3}d) = 3.1,$$

$$s_T = 5,$$

$$s_H = 2.$$

This model voltammogram (12) is quite similar to the one which has been obtained experimentally (3).

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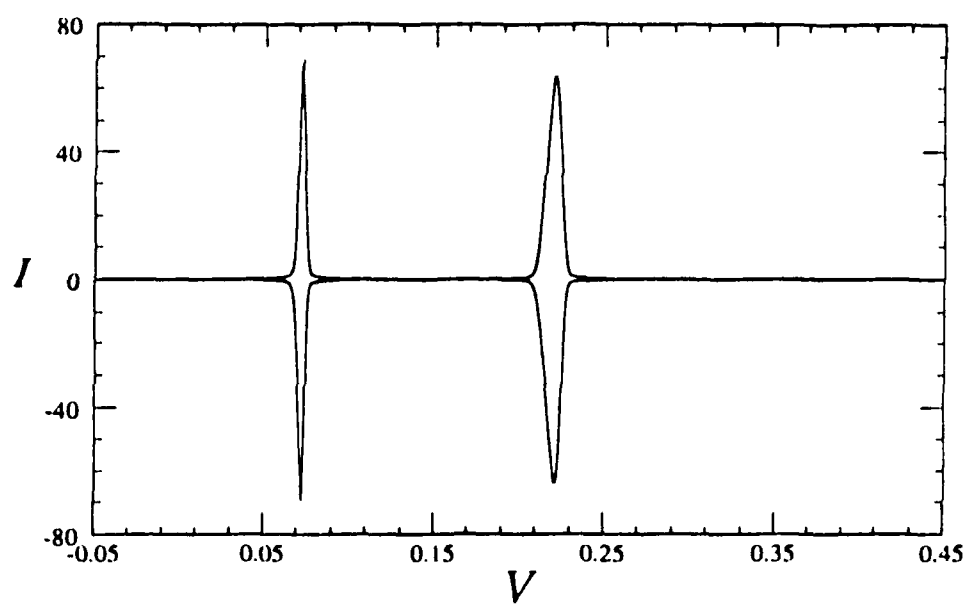


Figure 1. A model voltammogram for the underpotential deposition of copper on the (111) surface of gold. The current intensity is in units of $|dV/dt|$.